
Summary and Conclusions for Independent Lines of Evidence for Navy's Groundwater Chemistry Analysis

This document summarizes the 22 independent lines of evidence (presented by the Navy during the February 21, 2019 AOC Technical Working Group Meeting [webinar]) on interpretation of groundwater chemistry as it is related to 1) evidence of LNAPL in outlying wells, 2) evidence of impacts to Red Hill Shaft, and 3) evidence of groundwater impacts due to the 2014 release. Each primary line of evidence is also supported by multiple secondary lines of evidence. Unlike many contaminated sites, there are not significant concentrations of chemicals in monitoring wells. Rather, there are only extremely low levels that push the capabilities of most labs that need to be evaluated with caution. There are very few (if any) sites where such emphasis is put on such low-level concentrations.

Groundwater Chemistry as a Function of LNAPL Extent

- No conclusive evidence of measurable LNAPL in Red Hill wells.
- The presence of LNAPL near wells would exhibit both an organic and inorganic footprint (as seen relative to RHMW02).
- The Navy recognizes there is an LNAPL impact in groundwater upgradient of RHMW02 that occurred prior to the 2014 fuel release
- The presence of an LNAPL source in groundwater near a well would result in a continuing impact (chemical signature) to a well rather than random, sporadic, low-level detects.
- This chemical signature would exhibit the following:
 - An organic chemical signature consistent with the fuel type (e.g., jet fuel) and representative of dissolution of the LNAPL source over time (function of Raoult's Law) as well as weathering.
 - An inorganic chemical signature demonstrating biodegradation (e.g., low DO).
- Wells farther away from an LNAPL source would still see reduced concentrations of chemicals based on the factors mentioned above. The chemical signature would be significantly influenced by relative biodegradation of chemical constituents in the dissolved-phase plume (e.g., benzene would degrade relatively quickly as compared to heavier hydrocarbons).
 - Even in this case, it is highly unlikely that the chemical signature would result in random sporadic detections.

Summary of Key Issues

There are major issues with data quality and physical conditions in outlying wells including RHS that indicate no apparent impact from Red Hill Facility operations as follows:

- Lab dependency
 - frequency and locations regardless of concentration
 - Naphthalenes and PAHs in general
 - variability depending on method
 - TPH
- Oxidic environment
- Reducing conditions (ORP < 0 mV) are not present
- Methane not detected
- TICs and nonCOPCs are not remarkable as would be expected from a fuel release

Summary table: Primary and Secondary Lines of Evidence – Navy’s Groundwater Chemistry Evaluation

1. No evidence of nearby LNAPL in outlying wells

Primary LOE	Secondary LOEs
1a. Naphthalene (by itself) is not a good indicator for the presence of LNAPL	<div>i. There are sporadic detections of naphthalene at outlying wells. Incidence of detections correlates best with labs used rather than where detections occurred and at what concentrations.<ul style="list-style-type: none">Naphthalene detections during Q4 2012 to Q1 2015 (Calscience/Eurofins) are suspect.<ul style="list-style-type: none">Frequent detections of naphthalene from Q4 2012 to Q3 2014, then all detections stopped from Cal/Euro.<ul style="list-style-type: none">No coinciding detections of methylnaphthalenesThe lab that followed after Calscience (CAS/ALS) did not detect naphthalene at a similar frequencies or concentrations, even though the reporting limit was an order of magnitude lower.Approximately 60% of naphthalene detections in outlying wells occurred during the suspect period of Cal/Euro analysis. The remaining detections are highly sporadic.All naphthalenes were analyzed by EPA Method 8270 SIM at a time when only two ions were used to identify compounds. Three ions are required to have achieve robust identification.The very low detection limits for naphthalenes (e.g., 0.005 µg/L by CAS/ALS) are susceptible to interferences/artifacts and are inherently more variable.</div>
1b. Electron acceptors are not depleted at outlying wells	<div>i. Oxidic conditions are present at outlying wells<ul style="list-style-type: none">DO concentrations ranged from 5.09 to 9.31 mg/L (Q4 2018) at outlying wells that are representative of water table chemistry.<ul style="list-style-type: none">RHMW07, RHMW11, and Halawa Deep are not representative of water table chemistry.The range of DO in Red Hill outlying wells is generally consistent with observed DO in Oahu wells.Nitrate concentrations range from 2 to 5.5 mg/L (Q4 2018) at outlying wells that are representative of water table chemistry, demonstrating that nitrate is not depleted.Sulfate concentrations range from 6.9 to 51.3 mg/L (Q4 2018) at outlying wells that are representative of water table chemistry, demonstrating that nitrate is not depleted.Reducing conditions (ORP < 0 mV) are not present in outlying wells (Q4 2018).Apart from one sampling event at RHMW08, the ORP has been positive since Q4 2016 at outlying wells representative of the water table.</div>
1c. Metabolic byproducts are not present at outlying wells	<div>i. Methane was not detected in outlying wells (Q4 2018).<ul style="list-style-type: none">Methane has not been detected in outlying wells representative of water table chemistry since Q4 2016.</div> <div>ii. Ferrous iron was not detected in RHMW04, RHMW05, RHMW08, RHMW09, RHMW10, and was detected below the limit of quantitation at RHMW06 (0.16 J mg/L) (Q4 2018).<ul style="list-style-type: none">Since Q4 2016, ferrous iron has either been nondetect or below the limit of quantitation in outlying wells representative of water table chemistry.</div>
1d. There are not consistent coinciding detections of COPCs and nonCOPCs (e.g., BTEX, methylnaphthalene, nonpyrogenic PAHs) with naphthalene	<div>i. BTEX were not detected in RHMW06, RHMW07, RHMW08, RHMW09, RHMW10, or all levels of RHMW11.</div> <div>ii. BTEX were detected infrequently (1 to 5 times) at the remaining outlying wells over the monitoring period, which is more indicative of sampling/lab artifacts.<ul style="list-style-type: none">Concentrations were often below the limit of quantitation and ranged from 0.07 J to 3.8 µg/L.</div> <div>iii. NonCOPC detections in outlying wells consisted mainly of compounds that are not associated with fuel: phthalates, halogenated VOCs, acetone, oxygenated compounds, and pyrogenic PAHs.</div> <div>iv. NonCOPCs that can be present in fuels, such as non-pyrogenic PAHs, were detected infrequently in outlying wells; detections occurred in two samples in RHMW05 and RHMW07, and one sample in RHMW04, indicating sampling/lab artifact issues.<ul style="list-style-type: none">Non-pyrogenic PAHs were not detected in RHMW06, RHMW08, or RHMW09.</div>
1e. TPH should be assessed in the context of other COPCs and nonCOPCs, as trend analyses are difficult because of inconsistent methodology and labs	<div>i. TPH is a parameter defined by the method used.</div> <div>ii. TPH results can include hydrocarbons, metabolites/polar compounds and anything present that can be detected by the method.</div> <div>iii. TPH can be used as an indicator parameter for potential impact to GW, but the absolute values should be interpreted with caution. Changes can be method-, lab-related.<ul style="list-style-type: none">TPH detection is not a direct indication of hydrocarbons in GW.</div>

1. No evidence of nearby LNAPL in outlying wells

Primary LOE	Secondary LOEs
1f. TICs are not a good indicator of the presence of LNAPL in outlying wells	<div>i. TIC identification and concentrations cannot be confirmed without comparison to a known standard.</div> <div>ii. Majority of TIC detections are not associated with fuels: phthalates, halogenated compounds, oxygen containing compounds.<div>• These compounds are likely associated with sample/lab contamination, well construction/maintenance, historical activities at the site unrelated to fuel releases.</div></div> <div>iii. TIC hydrocarbon detections in outlying wells are only trimethylbenzenes.<div>• Trimethylbenzene would be expected to be found with other hydrocarbons if coming from a fuel/LNAPL; trimethylbenzene was the only TIC detected in outlying well samples.</div><div>• Trimethylbenzene was analyzed with Method 8260 in all outlying wells in 2017 and was not detected.</div></div>
1g. Lead scavengers (1,2-dibromoethane and 1,2-dichloroethane) were not detected in outlying wells except for 1,2-dichloroethane in RHMW08 in 2017	<div>i. 1,2-dichloroethane was used in motor gasoline (not aviation gasoline). Motor gasoline was stored in Tank 17 prior to 1968. It is likely the detections of 1,2-dichloroethane in RHMW08 are from either fumigants or PVC impurity rather than motor gasoline.</div> <div>ii. Based on dissolved lead analyses, there is no evidence of a leaded fuel release. To adequately evaluate lead in the environment, careful consideration should be given to the local range of background concentrations as well as filtering of water samples, since lead is a naturally occurring element.</div>

1a. No evidence of impact to other outlying wells from 2014 fuel release

1h. Continued sporadic detections of BTEX with no apparent increase in detection frequency after the 2014 fuel release	
1i. Continued sporadic detections of naphthalene with no apparent increase in detection frequency after 2014 fuel release	<div>i. Apparent decrease in naphthalene detection frequency in outlying wells after the period of Q4 2012 to Q3 2014 when Calscience/Eurofins stopped detecting naphthalene.</div>

2. No evidence of LNAPL nearby Red Hill Shaft

Primary LOE	Secondary LOEs
2a. Naphthalene (by itself) is not a good indicator of the presence of LNAPL near Red Hill Shaft	<div><div>i. There are sporadic detections of naphthalene at Red Hill Shaft<ul style="list-style-type: none">Naphthalene detections during Q4 2012 to Q1 2015 (Calscience/Eurofins) are suspect<ul style="list-style-type: none">Frequent detections of naphthalene from Q4 2012 to Q3 2014, then all detections stopped from Cal/Euro, indicating sampling/lab artifacts.<ul style="list-style-type: none">No coinciding detections of methylnaphthalenesThe lab that followed Calscience (CAS/ALS) did not detect naphthalene at a similar frequencies or concentrations even though the reporting limit was an order of magnitude lower.The concentrations of naphthalene detected during Q4 2012 to Q3 2014 were similar to the concentrations detected in other outlying wells (e.g., Halawa Deep, RHMW05). Similar concentrations would not be expected at these 3 wells with very different constructions<ul style="list-style-type: none">Red Hill Shaft – Induced flowHalawa Deep – Deep borehole with casing ~40 ft below regional aquiferRHMW05 – Standard monitoring wellAll naphthalenes were analyzed by EPA Method 8270 SIM at a time when only two ions were used to identify compounds. Three ions are required to have achieve robust identification.</div><div>ii. The very low detection limits for naphthalenes (e.g., 0.005 µg/L by CAS/ALS) are susceptible to interferences/artifacts and are inherently more variable.</div><div>iii. Naphthalene detections do not often coincide with 1- and 2-methylnaphthalene or TPH detections, as would be expected if the detections were due to a nearby LNAPL source.</div></div>
2b. Electron acceptors are not depleted at Red Hill Shaft	<div><div>i. Oxic conditions are present at Red Hill Shaft (DO = 8.7 mg/L during Q4 2018 sampling event).</div><div>ii. Nitrate was 2.3 mg/L during Q4 2018 sampling event and is not depleted.</div><div>iii. Sulfate was 15.6 mg/L during Q4 sampling event and is not depleted.</div><div>iv. Reducing conditions (ORP < 0 mV) were not present.</div></div>
2c. Metabolic byproducts (methane and ferrous iron) were not detected in Red Hill Shaft (Q4 2018)	<div><div>i. Methane has been non-detect in Red Hill Shaft since Q4 2016.</div><div>ii. Ferrous iron has been most commonly non-detect in Red Hill Shaft since Q4 2016, detected concentrations have ranged from 0.17 J to 0.34 mg/L.</div></div>
2d. There are not consistent coinciding detections of COPCs and nonCOPCs (e.g., BTEX, methylnaphthalene, nonpyrogenic PAHs) with naphthalene	<div><div>i. BTEX have been detected in two samples (Q4 2012 and Q2 2018) and were not confirmed during the subsequent sampling events.</div><div>ii. NonCOPC detections in Red Hill Shaft consisted mainly of compounds that are not associated with fuel: phthalates, halogenated VOCs, acetone, oxygenated compounds, and pyrogenic PAHs.</div><div>iii. NonCOPCs related to fuel, non-pyrogenic PAHs, were detected in only one sample from Red Hill Shaft in Q4 2005.</div></div>
2e. TPH should be assessed in the context of other COPCs and nonCOPCs as trend analysis is difficult because of inconsistent methodology and labs	<div><div>i. TPH detections often did not coincide with detections of other COPCs.</div><div>ii. TPH is a parameter defined by the method used.</div><div>iii. TPH results can include hydrocarbons, metabolites/polar compounds and anything present that can be detected by the method.</div><div>iv. TPH can be used as an indicator parameter or potential impact to GW, but the absolute values should be interpreted with caution. Changes can be method-, lab-related.</div><div>v. TPH detection is not a direct indication of hydrocarbons in GW.</div></div>
2f. TICs are not a good indicator of the presence of LNAPL in outlying wells	<div><div>i. TIC identification and concentrations cannot be confirmed without comparison to a known standard.</div><div>ii. Majority of TIC detections are not associated with fuel: phthalates, halogenated compounds, oxygen containing compounds.<ul style="list-style-type: none">These compounds may be associated with sample/lab contamination, well construction/maintenance, historical activities at the site unrelated to fuel releases.</div><div>iii. TIC hydrocarbon detections in Red Hill Shaft are of trimethylbenzene and two other hydrocarbons (1,2,3,4,5-Pentamethyl-Cyclopentane, and 2-Hexene, 3,5,5-Trimethyl-).<ul style="list-style-type: none">Trimethylbenzene would be expected to be found with other hydrocarbons if coming from a fuel/LNAPL; trimethylbenzene was the only TIC detected in outlying well samples.Trimethylbenzene was analyzed for with Method 8260 in Red Hill Shaft in 2017 and was not detected.The other TIC hydrocarbons were not detected in RHMW02 or RHMW01; detections are unlikely to be related to RHMW02.</div></div>
2g. Lead scavengers (1,2-dibromoethane and 1,2-dichloroethane) have not been detected in Red Hill Shaft	

3. No evidence of groundwater impact from 2014 fuel release

Primary LOE	Secondary LOEs
3a. BTEX detection occurrences did not change in RHMW02 after the 2014 fuel release	
3b. The ratio of methylnaphthalenes to naphthalene in RHMW02 did not change after the 2014 fuel release	<div>i. Fresh source of LNAPL in RHMW02 vicinity would change the ratio as fresh fuel has a different signature than degraded fuel.<ul style="list-style-type: none">In general, the parent PAH (COPC naphthalene) is less abundant than the sum of the corresponding alkylated PAHs (in this case, COPCs 1-methylnaphthalene and 2-methylnaphthalene, which are the two possible isomers on naphthalene with methyl group substitution) from any petroleum sources.</div>
3c. TPH alone not good indicator of changes in water chemistry at RHMW02 after 2014 release	<div>i. TPH should be assessed in context of other COPCs and nonCOPCs, as trend analysis is difficult because of inconsistent methodology and labs.<ul style="list-style-type: none">EPA Method 8015 is a guidance method, not prescriptive, and results in significant variation in analysis between labs.Changes in analytical lab often coincide with sharp changes in detected TPH concentrations in RHMW02.</div>
3d. Measured TPH concentrations in RHMW02 are not a good indicator of the presence of LNAPL	<div><div>i. Results can include hydrocarbons, metabolites/polar compounds, and anything present detectable by method.</div><div>ii. Concentrations/presence of TPH metabolites/polar compounds can be determined by using silica gel cleanup.</div><div>iii. Polar compounds are more soluble than parent nonpolar/hydrocarbons; therefore, presence of polar compounds/metabolites can result in increased solubility of what is measured as TPH.</div><div>iv. Polar compounds/metabolites in RHMW02 are more soluble than parent hydrocarbons; what is measured as TPH not indicative of presence of LNAPL from fresh release, but is indicative of an older nearby source.</div></div>
3e. COPC detection signature did not change in RHMW02 after the 2014 fuel release	<div>i. Increased number of sampling events immediately following 2014 fuel release results in an apparent increase in COPC detections. This is a result of more frequent sampling, not of a change in groundwater chemistry.</div>
3f. No lead scavengers (1,2-dibromoethane and 1,2-dichloroethane) were measured in RHMW02 before or after the 2014 fuel release	